

Photolysis of chlorsulfuron and metsulfuron-methyl in methanol

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Abstract: Photolysis of chlorsulfuron and metsulfuron-methyl was studied in methanol under UV light. Their rates of primary photolysis followed first-order kinetics. The main photoproducts were identified as 2-methoxy-4-methyl-1,3,5-triazin-6-amine, 2-chloro-benzenesulfonamide and methyl 2-(aminosulfonyl)benzoate, which entailed the cleavage of the two N–C ureic bonds. Further photolysis of benzenesulfonamide derivatives involved oxidation of $-\text{NH}_2$, cyclisation with loss of CH_3OH , and scission of the C–S bond. A trace of methyl *o*-mercaptobenzoate was also detected. The corresponding photolysis pathways of chlorsulfuron and metsulfuron-methyl were tentatively proposed.

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Keywords: chlorsulfuron; metsulfuron-methyl; photolysis; photoproducts; sulfonylurea

1 INTRODUCTION

In China chlorsulfuron [1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea; **1**], metsulfuron-methyl [methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate; **2**], and other sulfonylurea herbicides have been registered and widely used for weed control. The application area of chlorsulfuron is up to 2 million hectares, which is about 6% of the total sown area in China, and that of metsulfuron-methyl is about 1.4 million hectares.¹ The persistence and degradation of sulfonylurea herbicides have been among the research interests of environmental scientists.² In addition to pH- and temperature-dependent chemical hydrolysis and microbial breakdown, photolysis of sulfonylurea herbicides in water and in the adsorbed phase has been reported.^{3–6} Most of the photoproducts identified from irradiation involved cleavage of the sulfonylurea bridge.^{3,5,6}

To study the photochemical reactivity of pesticides on plant surfaces, organic solvents with selected functionalities (eg methanol, cyclohexane, acetone etc) as substitutes for components of plant waxes have been used in model photoreactions.⁷ Because of the polarity of sulfonylurea, we employed methanol as a simple model of the biomolecules. The aim of the present paper is to analyse photoproducts of chlorsulfuron and metsulfuron-methyl in methanol under UV light and give the possible reaction pathways.

2 MATERIALS AND METHODS

2.1 Materials

Chlorsulfuron (>99%) and metsulfuron-methyl (>99%) were provided by Prof Wenbin Zhang (Analytic Centre, Nanjing University). 2-Methoxy-4-methyl-1,3,5-triazin-6-amine (95%), 2-chloro-benzenesulfonamide (99%) and methyl 2-(aminosulfonyl)benzoate (99%), were gifts from Prof Nanxian Zhang (Department of Chemistry, Nanjing University). The purity of the above-mentioned chemicals was confirmed by HPLC. Other chemicals used were of analytical grade.

2.2 Photolysis of chlorsulfuron and metsulfuron-methyl

The ultraviolet-visible spectra of **1** and **2** were recorded on a Shimadzu UV-2201 UV-VIS spectrophotometer in methanol using a quartz cuvette (1 cm path length).

A solution of **1** (112 mg litre⁻¹) or **2** (137 mg litre⁻¹) in methanol was irradiated in quartz tubes with a low-pressure mercury lamp (20 W) and a water-cooled filter. Samples were withdrawn at intervals of 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 8, and 10 h for **1** and 0, 0.5, 1, 1.5, 2, 2.5, and 3.5 h for **2**. Temperature was controlled at 28 (±3) °C. The irradiated and dark control samples were analysed by HPLC on a Hypersil BDS C₁₈ (200 × 4.6 mm, 5 µm) column using methanol + water

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(60+40 by volume) as eluent, associated to a Hewlett Packard series 1050 chromatograph with UV detector (at 232nm).

To produce enough of the photoproducts for structural analysis, a solution of **1** or **2** was irradiated at a higher concentration (1 g litre^{-1}) in a cylindrical reactor equipped with a quartz filter and a mercury lamp at the axis.

2.3 Analysis of photoproducts

After irradiation for 10h, the solvent of a solution of **1** (1 g litre^{-1} , 250ml) was evaporated off under vacuum. The deposit was dissolved in ethyl acetate (2ml) and the supernatant liquid decanted and concentrated to less than 1 ml. This sample was sucked into the inner boundary of the round silica gel thin layer (Silica Gel GF₂₅₄, Qingdao Ocean Chem, China). The silica gel layer was 2mm thick, with the inner and outer boundary 2.5cm and 11.5cm away from the centre, respectively. During the centrifugal thin-layer chromatography experiment, the first circle of extract was eluted with ethyl acetate at a flow-rate increasing from 2 to 4 ml min^{-1} . The extracts from several replicate experiments were combined and purified by crystallisation from methanol and analysed by IR (Nicolet 170SX), ^1H NMR (Bruker-500) and mass spectroscopy. The other extracts and the above-generated insoluble residue were combined into a dichloromethane solution for GC-MS analysis.

A solution of **2** (1 g litre^{-1} , 250ml) was concentrated to about 1 ml on a rotary evaporation after irradiation for 3.5h. The solid deposit was crystallised three times from methanol as white needles, mp 257–258°C, and identified by IR, ^1H NMR and mass spectroscopy. The yellow liquid with an offensive smell was analysed by GC-MS. MS and GC-MS were recorded on a VG ZAB-MS instrument. The ionization potential was 70eV. The GC conditions were as follows: OV-101 fused silica capillary column; temperature programme 50°C to 120°C at 4°C min^{-1} . Helium was used as the carrier gas.

3 RESULTS

The UV spectra of **1** and **2** are similar, as shown in Fig 1. Their absorption maxima are at 232 and 223nm respectively, while the absorption at wavelengths higher than 300nm is very low. Thus a low-pressure mercury lamp (emission at 254nm) was selected to supply UV light in this study.

3.1 Rate of photolysis of chlorsulfuron and metsulfuron-methyl

Typical chromatograms of the irradiated solutions are given in Fig 2. The HPLC peaks in Fig 2 were qualitatively determined by comparison of the retention time to the standard samples.

The concentration of **1** and **2** decreased by 7.4% and 5.5%, respectively, during the dark control periods (10h and 3.5h for **1** and **2**, respectively). This

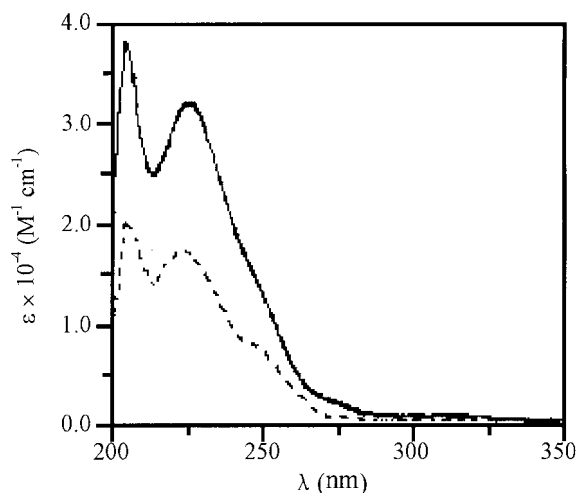


Figure 1. UV spectra of (---) chlorsulfuron and (—) metsulfuron-methyl.

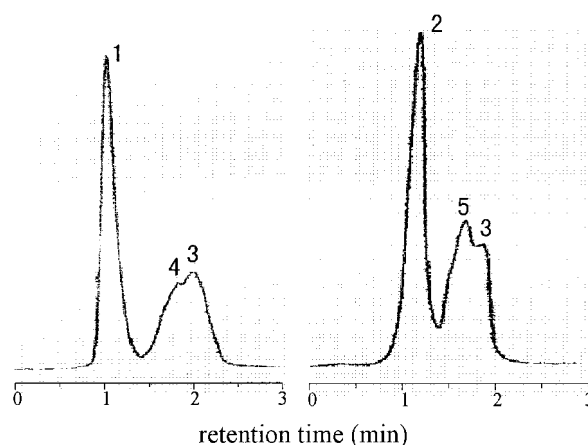


Figure 2. HPLC chromatograms of irradiated solutions of chlorsulfuron (**1**) and metsulfuron-methyl (**2**). Eluent methanol+water (60+40 by volume). Detection at 232nm.

indicates that **1** and **2** are quite stable under the conditions and time frame of this study and that the degradation observed in this study can mainly be attributed to photolysis.

The log percentage concentrations of **1** and **2**, plotted against time, resulted in a straight line, suggesting first-order rate kinetics with a statistically significant rate constant and high r value (Table 1). The photolysis half-lives of **1** and **2** were 6.3h and 1.8h, respectively.

3.2 Analysis of photoproducts

HPLC of irradiated solutions of **1** and **2** (Fig 2) showed that 2-methoxy-4-methyl-1,3,5-triazin-6-amine (**3**), 2-chloro-benzenesulfonamide (**4**) and

Table 1. Rate constant(k) and half-life ($t_{1/2}$) values for chlorsulfuron and metsulfuron-methyl in methanol under UV light

	n^a	$k\text{ (h}^{-1}\text{)}$	$t_{1/2}\text{ (h)}$	r^b
Chlorsulfuron	11	0.110	6.3	0.979
Metsulfuron-methyl	7	0.385	1.8	0.971

^a Number of sampling points.

^b Linear regression coefficient.

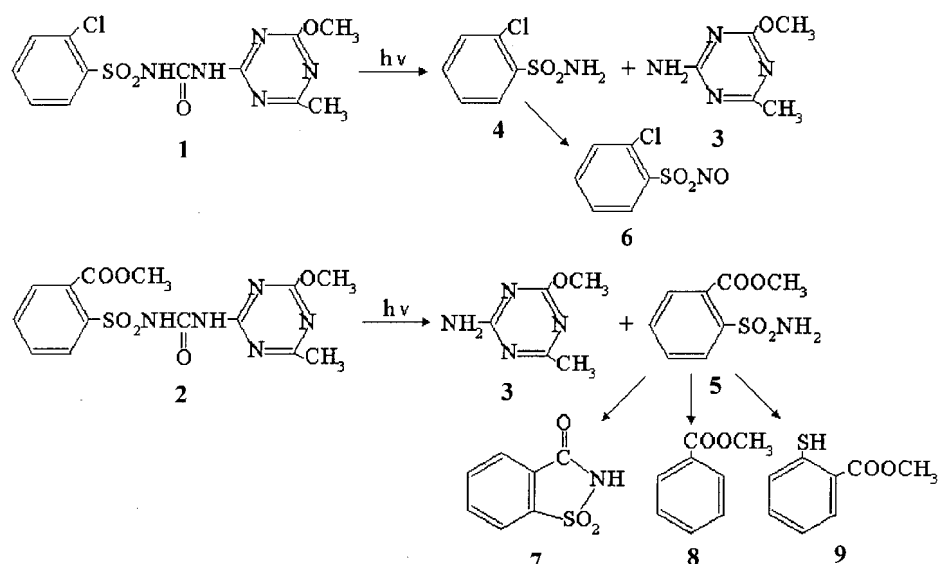


Figure 3. Proposed pathways for the photolysis of chlorsulfuron (1) and metsulfuron-methyl (2) in methanol.

methyl 2-(aminosulfonyl)benzoate (5) were photoproduced (Fig 3).

The analytical results of the extract from TLC were as follows:

IR: ν_{\max} 3350, 3250, 1555, 1335, 1160 cm^{-1} ; [^1H]NMR: δ 8.1 (s, 2H), 7.6 (m, 4H); MS: m/z 191 M^+ , fragment ions 175 ($-\text{NH}_2$), 156 ($-\text{Cl}$), 111 ($-\text{SO}_2\text{NH}_2$). We reported it as 2-chloro-benzenesulfonamide (4).

The white needles from the irradiated solution of 2 were identified as 2-methoxy-4-methyl-1,3,5-triazin-6-amine (3), on the basis of the following results: IR: ν_{\max} 3324, 3179, 1691, 1545, 1468 cm^{-1} ; [^1H]NMR: δ 7.2 (s, 2H), 4.0 (s, 3H), 2.5 (s, 3H); MS: m/z 140 M^+ , fragment ions 110 ($\text{M}^+ - 30$, $-\text{OCH}_3$), 69, 58.

According to GC-MS (Table 2), the structures of photoproducts were reported as follows: 3, 6 for 1 and 3, 5, 7, 8, 9 for 2, respectively (Fig 3). The above structures were inferred from MS libraries. Photoproducts 3 and 5 were major and 6–9 were minor.

4 DISCUSSION

The formation of 3 and 4 from 1 and 3 and 5 from 2 can be confirmed by HPLC of the irradiated solutions as well as the isolation and structural characterisation of photoproducts. It can be explained by the cleavage

of the two N–C ureic bonds, which is the typical degradation pathway of sulfonylurea herbicides. The three compounds (3, 4 and 5) also represent the most important metabolites of chlorsulfuron and metsulfuron-methyl in the environment^{3,8,9}

Previous work has identified 6 as a photoproduct of 1 in water.³ In this study, the product 6 was probably formed by oxidation of 4 in analogy to the photochemical generation of the nitrosoproduct from *N*-(4-chlorophenyl)benzenesulfonamide¹⁰

We have noticed that the alcoholysis of chlorsulfuron did not yield saccharin (7) according to Sabadie,¹¹ though saccharin was often reported as a hydrolysis product or metabolite of some sulfonylurea herbicides.^{5,9} In this study, we found that photoproduct 5 may undergo cyclisation with loss of CH_3OH to give saccharin.

Further photolysis of 5 yielded methyl benzoate (8) as well as 7. Weiss *et al* detected the C–S bond cleavage products of sulfonylureas under irradiation of a low-pressure Hg lamp (70 W).¹² They found that a *p*-amino group drastically increased the photochemical stability of the sulfonylurea.¹² Similarly, we attributed the stability of chlorsulfuron, in terms of C–S bond, to the *o*-chloro group. Methyl benzoate was reported as an intermediate of sulfometuron-methyl [methyl 2-(4,6-dimethylpyrimidin-2-ylcarbonylsulfamoyl)benzoate] during aqueous photolysis.⁵

Methyl *o*-mercaptobenzoate (9) has never been reported as a photoproduct of sulfonylurea herbicides. In this study, we found that traces of 9 were yielded through an unknown pathway and related the odour of the irradiated solutions to it.

Thus the reactions of 1 and 2 under UV light can be tentatively explained by the pathways shown in Fig 3.

Because constituents of plant cuticles often contain alcoholic groups, methanol or 2-propanol has been used as a simple model for the biomolecules.² The methanol experiment in this study may give a good insight into the basic photochemical possibilities of 1 and 2. The results, however, cannot necessarily be

Table 2. MS analysis of the products by UV irradiation of chlorsulfuron and metsulfuron-methyl in methanol

Product	m/z (above 40)
3	140, 110, 69, 58
4	191, 175, 156, 111
5	199, 184, 103, 92, 77
6	205, 175, 141, 111, 75
7	183, 119, 104, 92
8	136, 105, 77, 51
9	168, 136, 108, 69, 65

extrapolated to plant surfaces and should be confirmed under natural conditions.

5 CONCLUSION

The photochemical fate of chlorsulfuron (1) and metsulfuron-methyl (2) in methanol was investigated. They photolysed rapidly by UV light with the formation of 2-methoxy-4-methyl-1,3,5-triazin-6-amine (3) and derived benzenesulfonamides (4 and 5). These products were formed via cleavage of the sulfonylurea bridge. Benzenesulfonamides underwent further phototransformation through cyclisation with loss of methanol, scission of the C–S bond and oxidation of –NH₂. The rate of the primary photolysis of chlorsulfuron and metsulfuron-methyl in methanol followed first-order kinetics and indicated that the two herbicides might not be very persistent on plant surfaces.

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